Electronic Supporting Information

$AZn_2(BO_3)Si_2O_5$ (A= Rb, Cs): First Examples of $KBe_2BO_3F_2$ Structure Type in the Borosilicate Family Exhibiting Deep-ultraviolet Cutoff Edge

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Table S1. Crystal data and structure refinements for **$RbZn_2(BO_3)Si_2O_5$** and **$CsZn_2(BO_3)Si_2O_5$**.

Empirical formula	$RbZn_2(BO_3)Si_2O_5$	$CsZn_2(BO_3)Si_2O_5$
Formula weight	411.20	458.64
Crystal system	Orthorhombic	Orthorhombic
Space group, *Z*	$Cmc2_1$, 4	$Cmc2_1$, 4
Unit cell dimensions (Å)	*a* = 8.308(5)	*a* = 8.446(3)
	b = 19.345(14)	*b* = 19.494(7)
	c = 4.935(3)	*c* = 4.963(2)
Volume (Å^3)	793.19(9)	817.24(5)
Density (calc) (g/cm^3)	3.443	3.728
θ range for data collection (deg)	2.11-27.52	2.628-27.503
Limiting indices	$-10 \le h \le 10$, $-25 \le k \le 25$, $-6 \le l \le 6$	$-10 \le h \le 7$, $-25 \le k \le 24$, $-6 \le l \le 6$
Reflections collected/unique	9181/955 [R(int) = 0.0906]	9143/1003 [R(int) = 0.0668]
Data/restraints/parameters	955 / 13 / 71	1003 / 1 / 71
Completeness (%)	99.6	98.9
Goodness of fit on F_o^2	1.074	1.155
Final *R* indices [$F_o^2 > 2\delta(F_o^2)$][a]	R_1 = 0.0310, wR_2 = 0.0664	R_1 = 0.0260, wR_2 = 0.0626
R indices (all data)[a]	R_1 = 0.0332, wR_2 = 0.0677	R_1 = 0.0293, wR_2 = 0.0635
Largest diff. peak and hole (e/Å^3)	1.191 and -0.762	0.908 and -0.902
Absolute structure parameter	-0.070(13)	0.15(4)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. The final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **$RbZn_2(BO_3)Si_2O_5$** and **$CsZn_2(BO_3)Si_2O_5$**, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum for each atom in asymmetric unit.

$CsZn_2(BO_3)Si_2O_5$

Atom	x	y	z	U(eq)	**BVS**
Cs(1)	10000	6140(1)	3614(3)	24(1)	1.028
Zn(1)	8105(1)	7956(1)	3635(4)	13(1)	2.108
Si(1)	13141(2)	4544(1)	3556(16)	30(1)	4.327
B(1)	5000	7287(6)	3520(60)	13(2)	2.847
O(1)	15000	4425(5)	3550(50)	47(3)	2.112
O(2)	12255(5)	3854(2)	3700(30)	23(1)	2.146
O(3)	12602(8)	5048(8)	5980(40)	74(3)	2.257
O(4)	6426(7)	7322(3)	4881(11)	18(1)	1.943
O(5)	10000	7731(4)	5723(15)	18(2)	1.976

$RbZn_2(BO_3)Si_2O_5$

Atom	x	y	z	U(eq)	**BVS**
Rb(1)	10000	8832(1)	3975(1)	24(1)	0.834
Zn(1)	8075(1)	7034(1)	4051(1)	12(1)	2.072
Si(1)	13088(1)	10454(1)	3705(2)	25(1)	4.213
B(1)	5000	7729(2)	3918(11)	13(1)	2.949
O(1)	12141(2)	11142(1)	4232(5)	16(1)	2.002
O(2)	15000	10584(1)	3735(7)	26(1)	2.066
O(3)	12608(3)	9842(1)	5684(4)	31(1)	2.152
O(4)	6457(2)	7711(1)	5183(4)	19(1)	1.967
O(5)	10000	7275(2)	6060(5)	19(1)	2.046

Table S3. Selected bond distances (Å) and angles (deg) for **$RbZn_2(BO_3)Si_2O_5$** and **$CsZn_2(BO_3)Si_2O_5$**.

$CsZn_2(BO_3)Si_2O_5$

Cs(1)-O(2)#1	3.094(12)	Zn(1)-O(5)	1.957(4)
Cs(1)-O(2)#2	3.094(12)	Zn(1)-O(4)	1.980(6)
Cs(1)-O(2)#3	3.162(13)	Zn(1)-O(4)#7	1.980(6)
Cs(1)-O(2)#4	3.162(13)	Si(1)-O(2)	1.541(5)
Cs(1)-O(5)	3.273(8)	Si(1)-O(3)#2	1.574(18)
Cs(1)-O(3)	3.277(16)	Si(1)-O(1)	1.587(2)
Cs(1)-O(3)#5	3.277(16)	Si(1)-O(3)	1.618(17)
Cs(1)-O(3)#1	3.451(17)	B(1)-O(4)#9	1.383(16)
Cs(1)-O(3)#2	3.451(17)	B(1)-O(4)	1.383(16)
Zn(1)-O(2)#8	1.893(4)	B(1)-O(5)#7	1.39(3)
O(2)#1-Cs(1)-O(2)#2	76.0(4)	O(3)-Cs(1)-O(4)#6	118.9(3)
O(2)#1-Cs(1)-O(2)#3	179.0(3)	O(3)#5-Cs(1)-O(4)#6	156.6(3)
O(2)#2-Cs(1)-O(2)#3	104.98(14)	O(3)#1-Cs(1)-O(4)#6	123.9(3)
O(2)#1-Cs(1)-O(2)#4	104.98(14)	O(3)#2-Cs(1)-O(4)#6	98.4(2)
O(2)#2-Cs(1)-O(2)#4	179.0(3)	O(2)#1-Cs(1)-O(4)#7	53.57(12)
O(2)#3-Cs(1)-O(2)#4	74.1(3)	O(2)#2-Cs(1)-O(4)#7	78.71(16)
O(2)#1-Cs(1)-O(5)	104.40(13)	O(2)#3-Cs(1)-O(4)#7	126.08(12)
O(2)#2-Cs(1)-O(5)	104.40(13)	O(2)#4-Cs(1)-O(4)#7	101.50(15)
O(2)#3-Cs(1)-O(5)	75.01(13)	O(5)-Cs(1)-O(4)#7	52.87(15)
O(2)#4-Cs(1)-O(5)	75.01(13)	O(3)-Cs(1)-O(4)#7	156.6(3)
O(2)#1-Cs(1)-O(3)	134.2(3)	O(3)#5-Cs(1)-O(4)#7	118.9(3)
O(2)#2-Cs(1)-O(3)	82.6(4)	O(3)#1-Cs(1)-O(4)#7	98.4(2)
O(2)#3-Cs(1)-O(3)	46.6(3)	O(3)#2-Cs(1)-O(4)#7	123.9(3)
O(2)#4-Cs(1)-O(3)	96.9(4)	O(4)#6-Cs(1)-O(4)#7	37.74(17)
O(5)-Cs(1)-O(3)	120.1(3)	O(2)#8-Zn(1)-O(5)	120.6(4)
O(2)#1-Cs(1)-O(3)#5	82.6(4)	O(2)#8-Zn(1)-O(4)	107.5(2)
O(2)#2-Cs(1)-O(3)#5	134.2(3)	O(5)-Zn(1)-O(4)	106.3(3)
O(2)#3-Cs(1)-O(3)#5	96.9(4)	O(2)#8-Zn(1)-O(4)#7	110.2(5)
O(2)#4-Cs(1)-O(3)#5	46.6(3)	O(5)-Zn(1)-O(4)#7	105.9(3)
O(5)-Cs(1)-O(3)#5	120.1(3)	O(4)-Zn(1)-O(4)#7	105.45(19)
O(3)-Cs(1)-O(3)#5	84.3(5)	O(2)-Si(1)-O(3)#2	109.7(10)
O(5)-Cs(1)-O(3)#2	139.2(2)	O(2)-Si(1)-O(1)	110.7(4)
O(3)-Cs(1)-O(3)#2	43.32(7)	O(3)#2-Si(1)-O(1)	111.0(10)
O(3)#5-Cs(1)-O(3)#2	97.31(14)	O(2)-Si(1)-O(3)	111.0(10)
O(3)#1-Cs(1)-O(3)#2	79.1(5)	O(3)#2-Si(1)-O(3)	102.5(2)
O(2)#1-Cs(1)-O(4)#6	78.71(16)	O(1)-Si(1)-O(3)	111.7(10)
O(2)#2-Cs(1)-O(4)#6	53.57(12)	O(4)#9-B(1)-O(4)	121(2)
O(2)#3-Cs(1)-O(4)#6	101.50(15)	O(4)#9-B(1)-O(5)#7	119.4(10)
O(2)#4-Cs(1)-O(4)#6	126.08(12)	O(4)-B(1)-O(5)#7	119.4(10)

O(5)-Cs(1)-O(4)#6	52.87(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,z-1/2 #2 x,-y+1,z-1/2 #3 x,-y+1,z+1/2 #4 -x+2,-y+1,z+1/2

#5 -x+2,y,z #6 x+1/2,-y+3/2,z-1/2 #7 -x+3/2,-y+3/2,z-1/2 #8 x-1/2,y+1/2,z

#9 -x+1,y,z #10 -x+3/2,-y+3/2,z+1/2 #11 -x+3,y,z #12 x+1/2,y-1/2,z

$RbZn_2(BO_3)Si_2O_5$

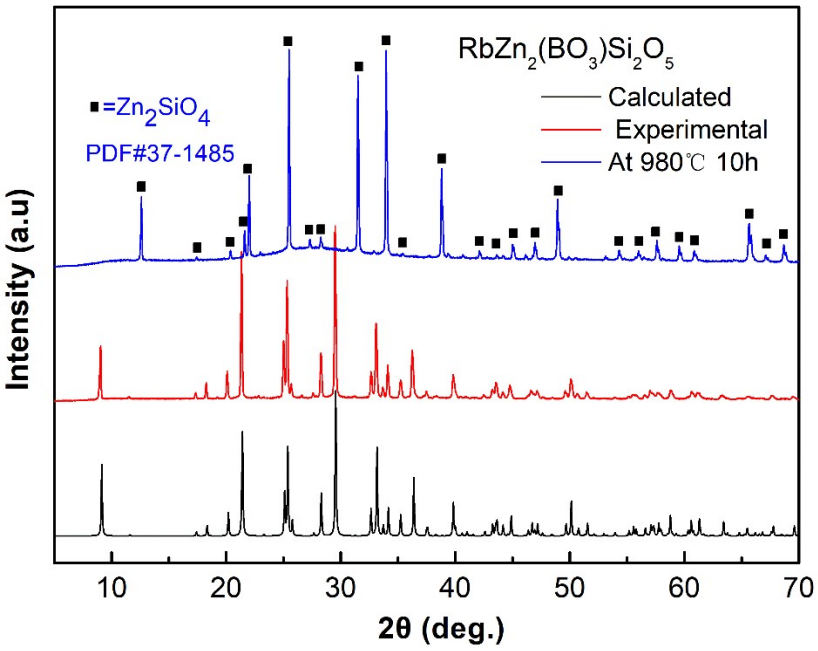
Rb(1)-O(1)#1	2.940(2)	Zn(1)-O(4)	1.9575(19)
Rb(1)-O(1)#2	2.940(2)	Zn(1)-O(4)#7	2.0096(19)
Rb(1)-O(3)#3	3.038(2)	Si(1)-O(1)	1.5683(16)
Rb(1)-O(3)	3.038(2)	Si(1)-O(3)	1.585(2)
Rb(1)-O(1)#4	3.146(2)	Si(1)-O(2)	1.6082(8)
Rb(1)-O(1)#5	3.146(2)	Si(1)-O(3)#2	1.647(2)
Rb(1)-O(5)	3.182(3)	B(1)-O(4)#9	1.362(3)
Zn(1)-O(1)#6	1.8940(15)	B(1)-O(4)	1.362(3)
Zn(1)-O(5)	1.9384(15)	B(1)-O(5)#7	1.410(6)
O(1)#1-Rb(1)-O(1)#2	74.45(8)	O(3)-Rb(1)-O(5)	121.29(5)
O(1)#1-Rb(1)-O(3)#3	77.21(5)	O(1)#4-Rb(1)-O(5)	75.43(5)
O(1)#2-Rb(1)-O(3)#3	129.91(5)	O(1)#5-Rb(1)-O(5)	75.43(5)
O(1)#1-Rb(1)-O(3)	129.91(5)	O(1)#6-Zn(1)-O(5)	122.21(10)
O(1)#2-Rb(1)-O(3)	77.21(5)	O(1)#6-Zn(1)-O(4)	108.31(8)
O(3)#3-Rb(1)-O(3)	91.01(9)	O(5)-Zn(1)-O(4)	105.07(9)
O(1)#1-Rb(1)-O(1)#4	176.64(6)	O(1)#6-Zn(1)-O(4)#7	110.34(9)
O(1)#2-Rb(1)-O(1)#4	108.31(5)	O(5)-Zn(1)-O(4)#7	105.49(9)
O(3)#3-Rb(1)-O(1)#4	99.46(5)	O(4)-Zn(1)-O(4)#7	103.88(6)
O(3)-Rb(1)-O(1)#4	50.03(5)	O(1)-Si(1)-O(3)	113.91(12)
O(1)#1-Rb(1)-O(1)#5	108.31(5)	O(1)-Si(1)-O(2)	111.21(12)
O(1)#2-Rb(1)-O(1)#5	176.64(6)	O(3)-Si(1)-O(2)	111.05(15)
O(3)#3-Rb(1)-O(1)#5	50.03(5)	O(1)-Si(1)-O(3)#2	108.93(12)
O(3)-Rb(1)-O(1)#5	99.46(5)	O(3)-Si(1)-O(3)#2	103.68(7)
O(1)#4-Rb(1)-O(1)#5	68.87(7)	O(2)-Si(1)-O(3)#2	107.58(16)
O(1)#1-Rb(1)-O(5)	105.86(5)	O(4)#9-B(1)-O(4)	125.3(4)
O(1)#2-Rb(1)-O(5)	105.86(5)	O(4)#9-B(1)-O(5)#7	117.3(2)
O(3)#3-Rb(1)-O(5)	121.28(5)	O(4)-B(1)-O(5)#7	117.3(2)

Symmetry transformations used to generate equivalent atoms:

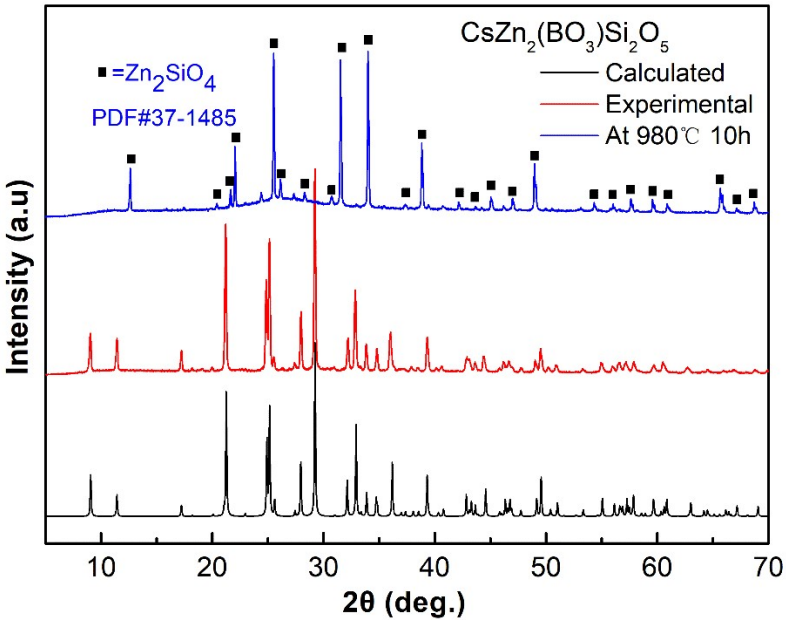
#1 -x+2,-y+2,z-1/2 #2 x,-y+2,z-1/2 #3 -x+2,y,z #4 x,-y+2,z+1/2

#5 -x+2,-y+2,z+1/2 #6 x-1/2,y-1/2,z #7 -x+3/2,-y+3/2,z-1/2

#8 -x+3/2,-y+3/2,z+1/2 #9 -x+1,y,z #10 x+1/2,y+1/2,z #11 -x+3,y,z



(a)



(b)

Figure S1. Powder XRD patterns of (a) $RbZn_2(BO_3)Si_2O_5$, and (b) $CsZn_2(BO_3)Si_2O_5$.

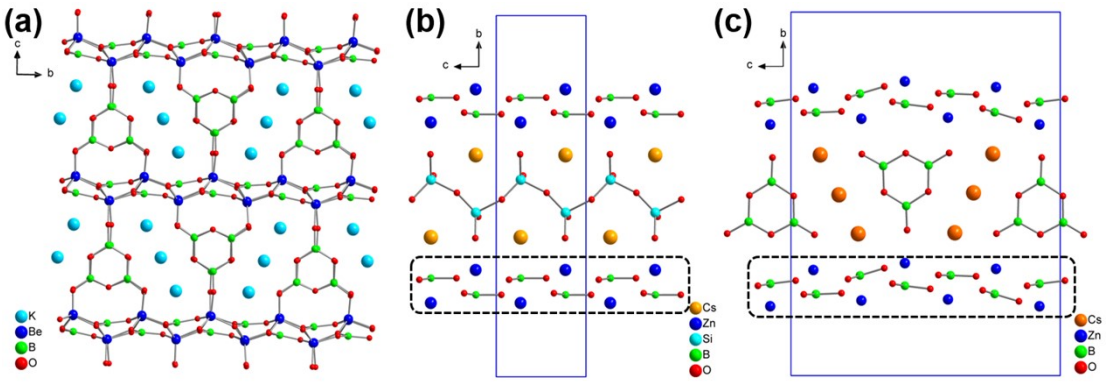


Figure S2. (a) 3D crystal structure of *γ*-$KBe_2B_3O_7$ view along the *a* axis, (b) alignment pattern of BO_3 groups in the crystal structure of $CsZn_2(BO_3)Si_2O_5$, (c) and alignment pattern of BO_3 groups in the crystal structure of $Cs_3Zn_6B_9O_{21}$.

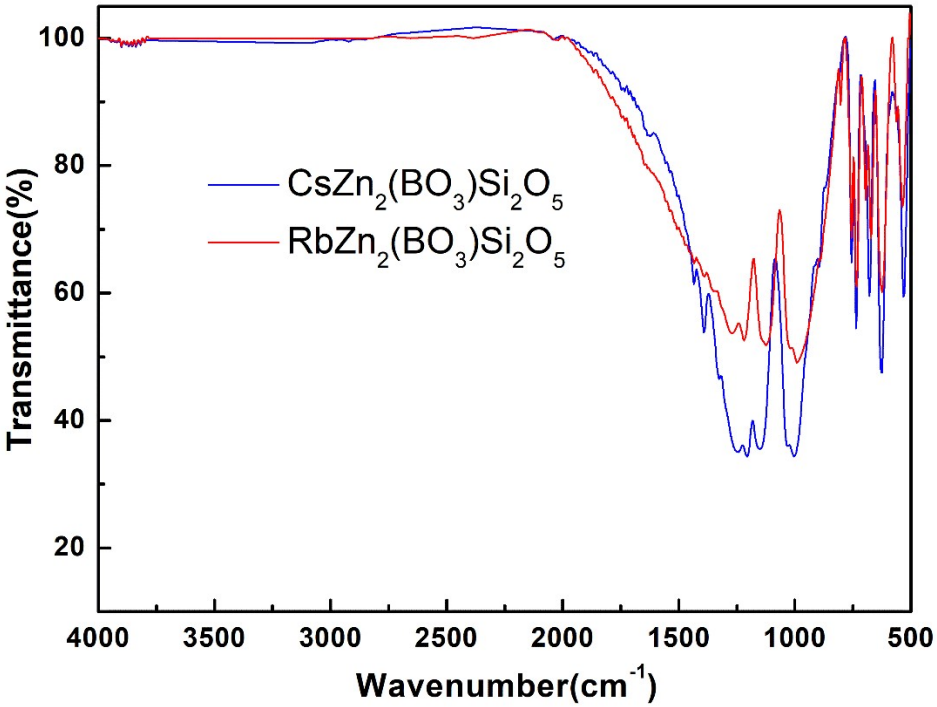


Figure S3. IR spectra of $RbZn_2(BO_3)Si_2O_5$ (red), and $CsZn_2(BO_3)Si_2O_5$ (blue).

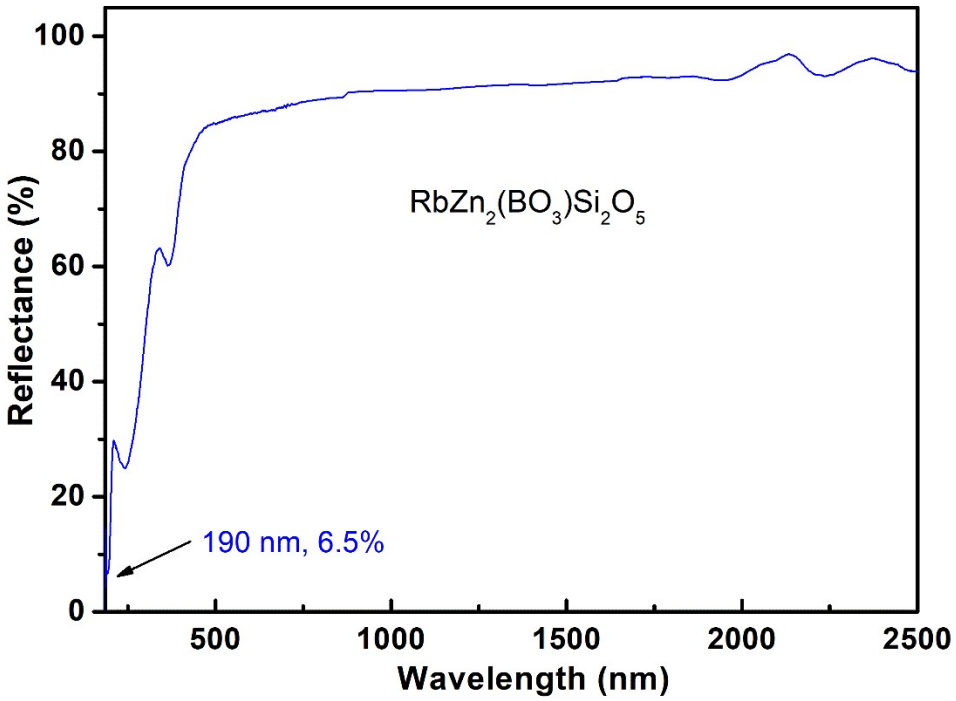


Figure S4. UV−vis−NIR diffuse reflectance spectrum of $RbZn_2(BO_3)Si_2O_5$.

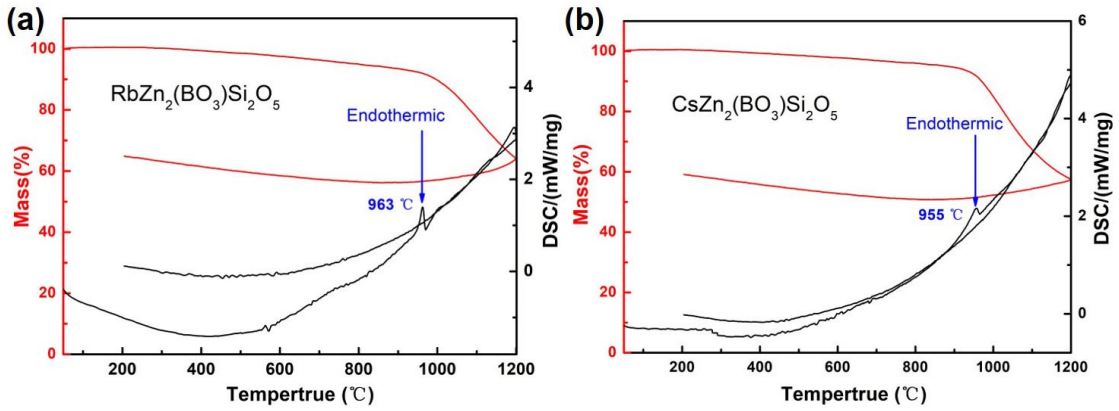


Figure S5. The TG-DSC curves of polycrystalline samples of $RbZn_2(BO_3)Si_2O_5$ (a), and $CsZn_2(BO_3)Si_2O_5$ (b).

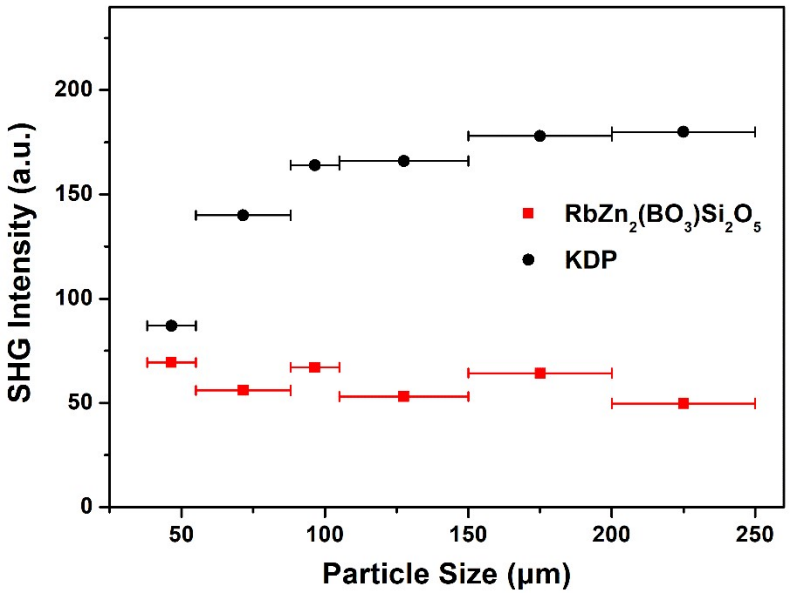


Figure S6. Powder SHG measurements for KDP, and $RbZn_2(BO_3)Si_2O_5$ (at 1064 nm, Q-switched Nd: YAG laser).

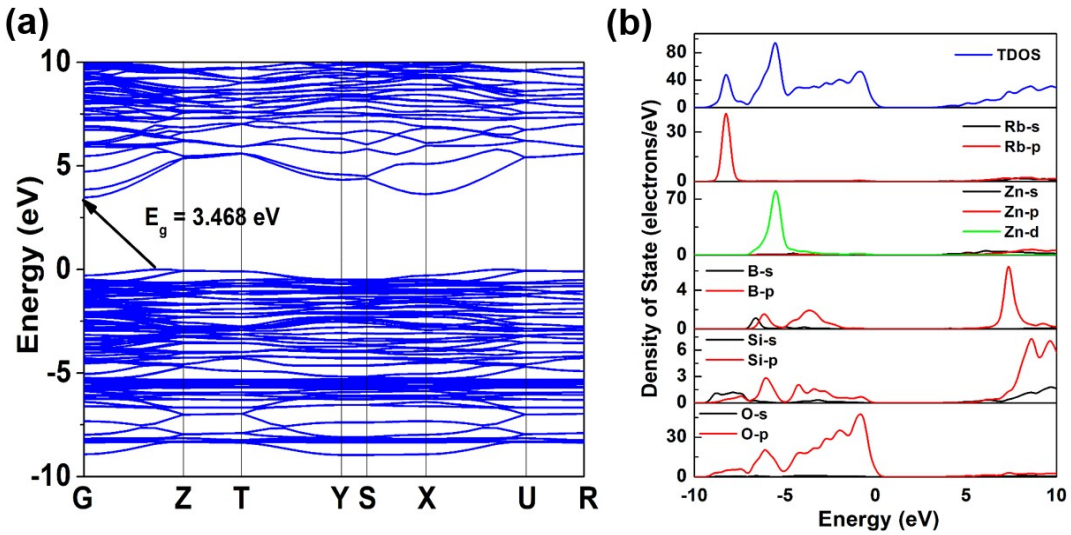


Figure S7. Calculated electronic band structure (a), total and partial densities of states (b), of $RbZn_2(BO_3)Si_2O_5$.

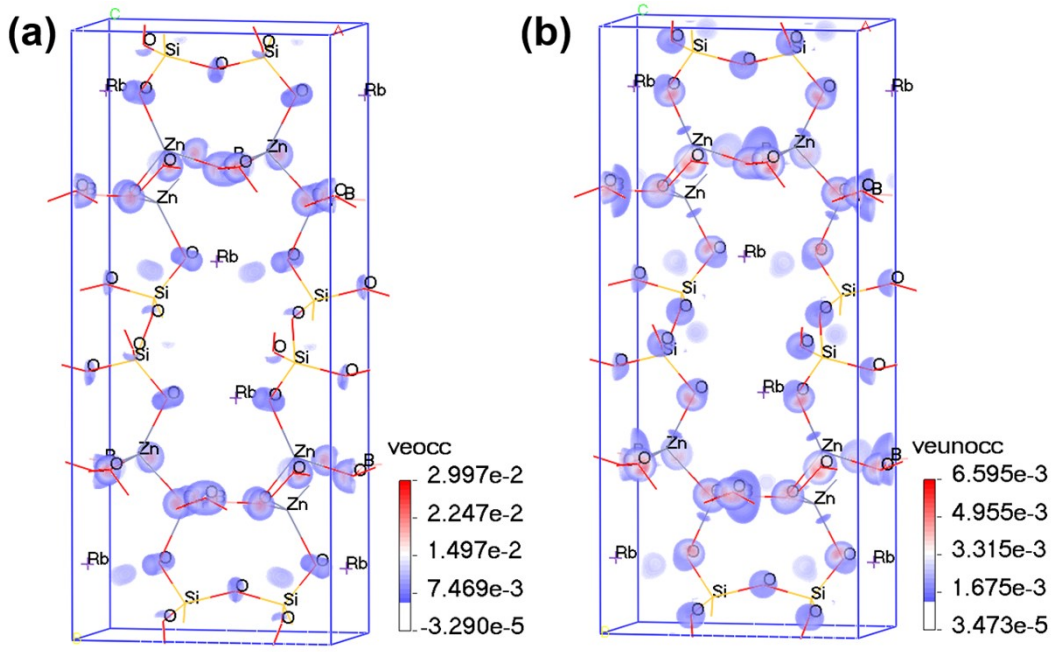


Figure S8. SHG density of occupied (a), and unoccupied (b) for $RbZn_2(BO_3)Si_2O_5$.

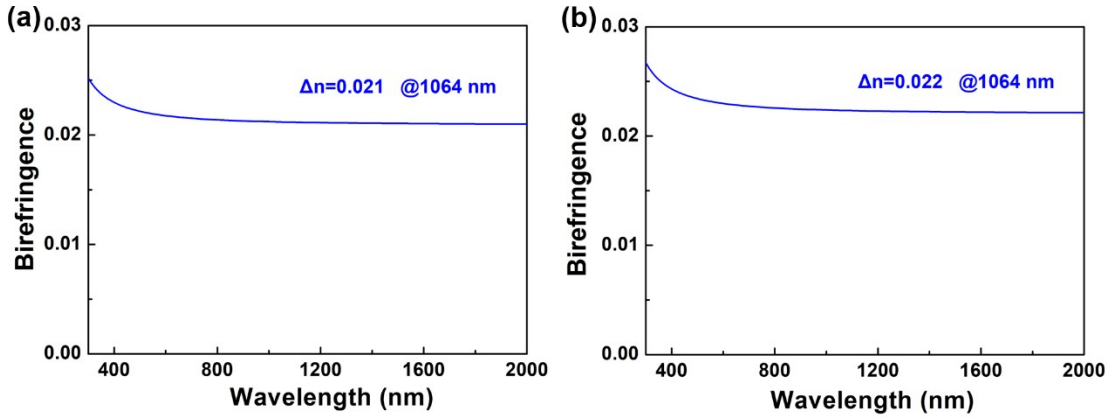


Figure S9. Calculated birefringence curves for $RbZn_2(BO_3)Si_2O_5$ (a), and $CsZn_2(BO_3)Si_2O_5$ (b).